

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 July 2003 (24.07.2003)

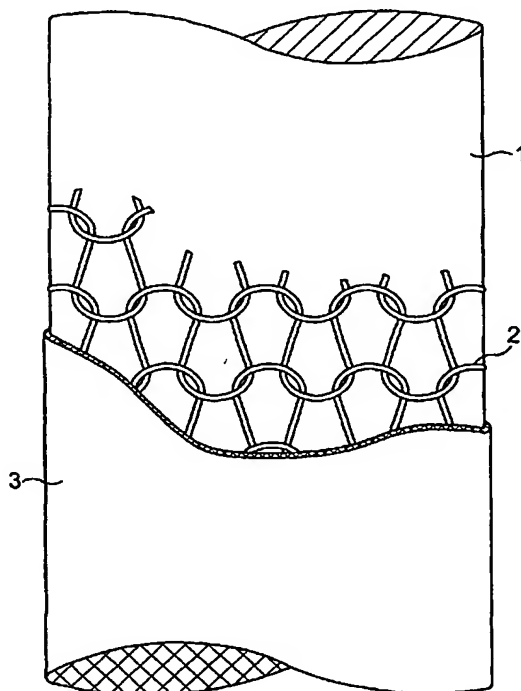
PCT

(10) International Publication Number
WO 03/059826 A1

- (51) International Patent Classification⁷: **C03B 5/167**
- (21) International Application Number: **PCT/GB03/00068**
- (22) International Filing Date: **10 January 2003 (10.01.2003)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
0200758.1 15 January 2002 (15.01.2002) **GB**
- (71) Applicant (for all designated States except US): **JOHN-SON MATTHEY PUBLIC LIMITED COMPANY**
[GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).
- (72) Inventor; and
(75) Inventor/Applicant (for US only): **DOYLE, Mark, Laurence** [GB/GB]; 2 Tuthill Court, Therfield, NR Royston, Herts SG8 9TT (GB).
- (74) Agent: **WISHART, Ian, Carmichael**; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).
- (81) Designated States (national): **JP, KR, US.**
- (84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR).
- Published:
— with international search report

[Continued on next page]

(54) Title: **PLATINUM METAL BASED ARTICLE FOR HIGH TEMPERATURE APPLICATIONS**



(57) Abstract: A high temperature article, such as for use in a device such as a stirrer suitable for containing molten glass, has a base metal component (1), a knitted Pt Gauze layer (2), and an outer Pt cladding (3). The device exhibits resistance to attack by molten glass and resistance to interdiffusion between the Pt cladding and the base metal. Preferably a knitted or woven Pt or Pt alloy fabric is used as a diffusion limiting layer between the base metal part and the other Pt cladding or protective layer.

WO 03/059826 A1

0 03/059826 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

HIGH TEMPERATURE DEVICES AND ARTICLES

5 This invention concerns high temperature device and articles, meaning especially devices and articles used at molten glass temperatures, and which need to be protected from attack by molten glass.

10 In the glass industry, homogenising and gobbing stirrers are used. These parts require excellent high temperature strength at glass forming temperatures, which are generally in the range 1000 to 1250°C. The traditional material chosen for such parts is molybdenum (Mo) which is clad in platinum foil. Although Mo is resistant to molten glass, it is rapidly oxidised and volatilised in contact with air at temperatures above 700°C. To avoid oxidation, the Pt cladding must completely contain the Mo core and the space between the Pt cladding and the
15 Mo part is evacuated to remove any oxygen. However, any direct contact between the Mo core and Pt cladding at elevated temperatures allows rapid inter-diffusion, so that the protection offered by the Pt cladding is compromised over time. It is therefore conventional to provide a protective coating on the Mo part, such as a sprayed ceramic, to act as a diffusion barrier. Such a multi-step construction adds complication and cost.

20 In recent years, oxide dispersion strengthened ("ODS") alloys have become available (examples include PM1000, PM2000, , MA758, MA956) with adequate high temperature strengths to act as stirrer cores for use in molten glass. Unlike Mo, these ODS materials do not catastrophically oxidise, but form relatively protective surface oxide layers. However,
25 these ODS materials are not resistant to molten glass and therefore still require protection in the form of Pt cladding. The Pt cladding does not have to be a complete containment because of the greater resistance of the core material to oxidation. Interdiffusion remains a problem if the Pt and ODS materials are in direct contact. Unfortunately, the best types of ceramic interlayers which could be considered as a diffusion barriers, do not have expansion
30 coefficients which match the requirements of the ODS alloys. Accordingly, these diffusion barrier layers can become damaged and spall off in service. In particular, the possibility of using part claddings (an opportunity to reduce cost) requires that the diffusion barrier layer extend right up to (or just beyond) the free edge of the cladding. This is a vulnerable point

because if spalling of the interlayer did occur it could cause contamination of the glass.

There remains a need for a protected article which does not suffer significant interdiffusion yet retains adequate strength in a glass furnace. It is also an advantage if the interlayer is flexible under the conditions of operation such that it does not crack, crumble or spall.

Accordingly, the present invention provides a high temperature article comprising a base metal part and a platinum group metal ("PGM") protective layer, separated by a diffusion limiting layer, characterised in that the diffusion limiting layer is a foraminate PGM structure.

Desirably, the foraminate PGM structure is a relatively low-density fabric, including woven or knitted fabrics, felts and sintered non-woven fabrics. It should be understood that other structures are included within the broadest scope of the invention. These may be highly expanded PGM sheet, PGM sheets with impressed "pimples", and others. However, the presently preferred structure is a knitted PGM fabric. We refer to Johnson Matthey USP 5,266,293 which discloses the manufacture of such knitted fabrics as catalyst gauzes, especially for ammonia oxidation. Such knitted PGM fabrics are commercially available.

The PGM protective layer is preferably Pt or a Pt alloy. The foraminate PGM structure is preferably Pt or a Pt alloy. The preferred non-woven structures are made from thread or wire of approximately 50- 85 μm diameter or from ribbon.

Preferred PGM structures have open areas of 60% or more and densities in the range 250-1200g/m². This permits air circulation, which has benefits with ODS materials in maintaining stable, protective oxide layers and also limits points of direct PGM-base metal contact. Knitted structures have additional advantages including flexibility, so that they can readily conform to the shape of the underlying part, which may be a stirrer with a complex external screw. A knitted PGM fabric has minimal contact points so that any diffusion has to

be through the contact points and multiple thin wires or ribbon, thus reducing diffusion of species from the PGM protective layer to the base metal part and *vice versa*.

5 A preferred base metal part is made from ODS material such as that marketed as PM2000 (Plansee Metals Ltd).

The invention will now be described by way of example and with reference to the accompanying schematic drawing.

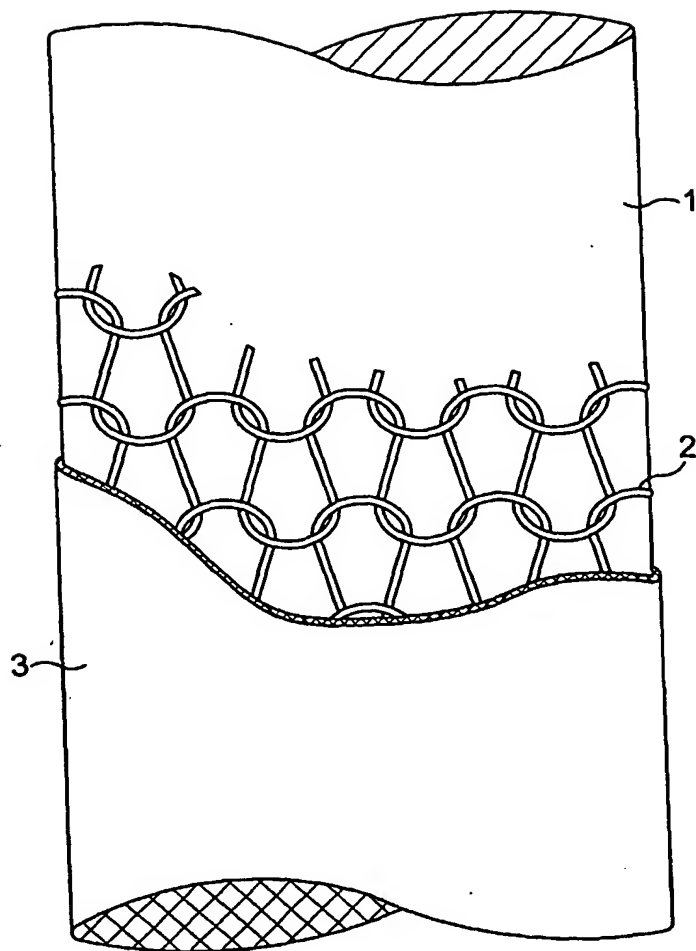
10 A PM2000 ODS part, 1, has a knitted Pt-5%Rh gauze (JM 'Nitroluk'), 2, applied thereto and fixed in place by hammer welding. Gauze 2 is knitted on a commercial knitting machine from 76 μm Pt-Rh wire to a weight of 620g/m². Fitted over the Pt gauze is a Pt cladding 3, constructed from 1mm thick Pt sheet by traditional methods.

15 A test article according to the invention has been tested in contact with molten glass for 1500 hours without failure or evidence of appreciable interdiffusion.

The skilled person will be able to modify and optimise the invention without departing from its scope.

CLAIMS

1. A high temperature article comprising a base metal part and a platinum group metal ("PGM") protective layer, separated by a diffusion limiting layer, characterised in that the diffusion limiting layer is a foraminate PGM structure.
5
2. An article according to claim 1, wherein the foraminate PGM structure is a fabric made from wire or ribbon.
- 10 3. An article according to claim 1 or 2, where both the PGM protective layer and the foraminate PGM structure are Pt or a Pt alloy.
4. An article according to claim 3, wherein the foraminate PGM structure is a layer of knitted or woven Pt wire or ribbon.
- 15 5. An article according to any of the preceding claims, wherein the base metal part is formed from ODS materials including PM2000, PM1000, MA758, MA956.
6. An article according to any of the preceding claims, in the form of a homogenising or gobbing stirrer or other metallic part for use in a glass furnace.
20
7. A diffusion limiting layer for use in the article of claim 1, formed from a knitted or woven Pt or Pt alloy fabric.



INTERNATIONAL SEARCH REPORT

PCT/GB 03/00068

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03B5/167

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 364 153 A (JOHNSON MATTHEY PLC) 18 April 1990 (1990-04-18) cited in the application the whole document ---	7
A	DE 43 26 143 A (BÖTTGER D) 9 December 1993 (1993-12-09) page 1, line 19 - line 26 ---	1
A	DE 199 41 610 C (W C HERAEUS GMBH & CO KG) 5 April 2001 (2001-04-05) column 2, line 1 - line 29 ---	1
A	EP 1 151 969 A (PLANSEE AG) 7 November 2001 (2001-11-07) column 5, line 3 - line 10; figure 2 column 5, line 38 - line 44 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

7 April 2003

Date of mailing of the international search report

15/04/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Stroud, J

INTERNATIONAL SEARCH REPORT

PCT/GB 03/00068

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 10, 10 October 2002 (2002-10-10) & JP 2002 167674 A (FURUYA KINZOKU:KK), 11 June 2002 (2002-06-11) abstract	1
P,A	DE 101 17 664 C (SCHOTT GLAS) 25 July 2002 (2002-07-25) claims 1-4	1

INTERNATIONAL SEARCH REPORT

PCT/GB 03/00068

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0364153	A	18-04-1990	AT 73010 T	15-03-1992
			AU 612906 B2	18-07-1991
			AU 4280489 A	26-04-1990
			CA 2000349 A1	12-04-1990
			DE 68900928 D1	09-04-1992
			DK 504089 A	13-04-1990
			EG 18939 A	28-02-1994
			EP 0364153 A1	18-04-1990
			ES 2037959 T3	01-07-1993
			FI 92806 B	30-09-1994
			GR 3003971 T3	16-03-1993
			IE 62512 B1	08-02-1995
			IL 91944 A	08-07-1993
			IN 176584 A1	03-08-1996
			JP 2216247 A	29-08-1990
			MX 172395 B	15-12-1993
			NO 894063 A	17-04-1990
			PT 91967 A	31-05-1990
			TR 26719 A	06-07-1994
			US 5266293 A	30-11-1993
			US 5188813 A	23-02-1993
			YU 198089 A1	30-04-1991
			ZA 8907707 A	29-08-1990
DE 4326143	A	09-12-1993	DE 4326143 A1	09-12-1993
DE 19941610	C	05-04-2001	DE 19941610 C1	05-04-2001
EP 1151969	A	07-11-2001	AT 4238 U1	25-04-2001
			EP 1151969 A2	07-11-2001
			JP 2002020125 A	23-01-2002
			US 2002014093 A1	07-02-2002
JP 2002167674	A	11-06-2002	NONE	
DE 10117664	C	25-07-2002	DE 10117664 C1	25-07-2002
			JP 2002362928 A	18-12-2002